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σ2P,O-hybrid ligands: Synthesis of the first 4-hydrox--1,3-benzazaphospholes by ortho-lithiation of M-amidophenyl diethyl phosphates

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Abstract

Copyright © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. The m-phosphorylanilides 2 are available from anilides 1 by the Atherton-Todd reaction; the selective ortho-lithiation of the o'-methyl-protected phosphorylpivalanilide 2b with tBuLi proceeded in high yield in the presence of ClSiMe3. The ortho-lithiation is followed by rapid 1,3-migration of the PO3Et2 group to yield the phosphonoanilide cis/trans-3b. This compound mainly reacts with excess LiAlH4 by reductive cyclization to form the 4-hydroxy-1H-1,3-benzazaphosphole 6. The lithiation of the o'-unprotected phosphorylpivalanilide 2a with LDA was unselective and led to 3a and 4a in low yields, whereas additional ortho-lithiation of the benzoyl group occurred for the lithiation of the o'-protected phosphonobenzanilide 2c with tBuLi/LDA to give 7 in rather low yield. The reduction of crude 7 led to (benzylamino)phenol 8 and the 4-hydroxy-1H-1,3-benzazaphosphole 9 as a minor product. The properties, NMR spectroscopy data, and crystal structures of 5b, 6, and 8 are reported.

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Keywords

Amides, Lithiation, Phosphorus heterocycles, Phosphorylation, Rearrangement